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X-Ray Study of the Cyclohexaamylose-Iodine Complex

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By William J. James and Dexter French

Introduction

The action of Bacillus macerans upon starch solutions has led to the isolation of crystalline dextrins by F. Schardinger (1). They are chemically homogenous and react readily with iodine to form both brown and blue colored complexes analogous to the starch-iodine complex. The Schardinger dextrins have been shown to be cyclic (2) and made up entirely of glucose residues bonded by α– 1, 4 - glucosidic linkages as in amylose. One of these, cyclohexaamylose (Schardinger's α– dextrin), containing as the name implies, six glucose units, reacts with iodide-free iodine in aqueous solution to form a stable crystalline complex.

X-ray investigations have been carried out upon this complex to obtain evidence concerning the structural configuration of a compound closely analogous to the amylose-iodine complex.

Struture Determination

Preparation of the complex.—Finely powdered iodine was heated with cyclohexaamylose in aqueous solution. The red-brown complex which crystallized on cooling was filtered and washed with water.

Analysis: Calculated for $(C_6H_{10}O_5)_6 \cdot I_2 \cdot 14H_2O$: I = 17.2%, $(C_6H_{10}O_5)_6$ = 65.7%, H_2O = 17.1%.

Observed: I = 17.5%, $(C_6H_{10}O_5)_6$ (by optical rotation) = 64.9%, H_2O (by difference) = 17.6%.

Physical Data.—Crystals of the cyclohexaamylose-iodine complex are orthorhombic needles with lattice constants, a_0 = 14.38Å, b_0 = 36.07Å, and c_0 = 9.43Å. The calculated density for four molecules per unit cell is 1.99.

Examination of the crystalline complex under the polarizing microscope indicated little or no dichroism when the light was parallel to the x axis. With the light parallel to the y axis, the crystals were dichroic changing in color from light amber to orange red; light was absorbed at a maximum when the electric vector was parallel to the z axis. With the light parallel to the z axis, the crystals were

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again dichroic with the absorption of light maximum when the electric vector was parallel to the y axis.

From the above it can be concluded that the iodine molecule axis is parallel to the (100) plane and inclined at approximately 45° to the y axis.

X-ray diagrams obtained by Weissenberg and precession tech-

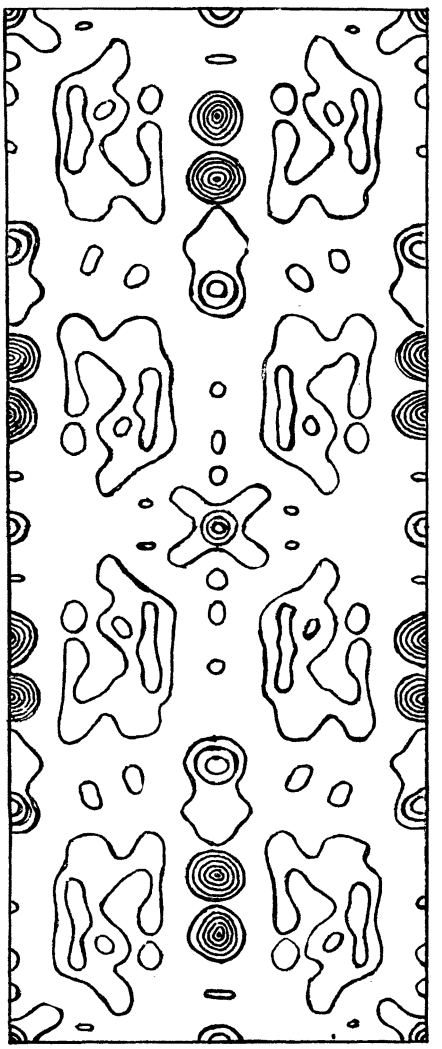

Figure 1. Fourier Projection onto the (001) Plane.

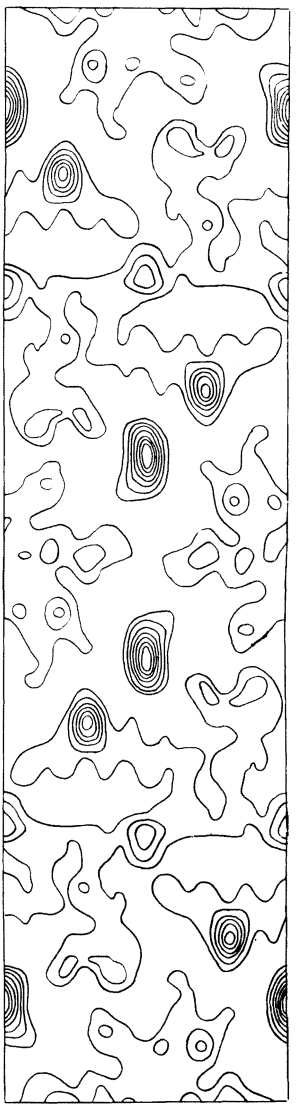

Figure 2. Fourier Projection onto the (100) Plane.

niques showed all odd orders of the (h00), (0k0), and (001) absent through (12 0 0), (0 32 0), and (0 0 8). No other systematic extinctions were found. Since the material is optically active, the space group is D_2^4—$P2_12_12_1$.

Determination of Parameters.—Complete three-dimensional data were obtained using CuKα radiation and a Weissenberg camera. Intensities of the reflections were estimated visually from timed exposures and multi-film photographs.

The intensities were corrected for Lorentz and polarization factors and then used to obtain the Patterson function projected onto the (001), (100), (010) planes and the Harker function projected onto the (100) plane for varying intervals along the x axis. The iodine parameters obtained from both the three-dimensional and two-dimensional projections are as follows: $x_1 = x_2 = 15/60$, $y_1 = 9.2/60$, $y_2 = 5.6/60$, $z_1 = 30/60$, and $z_2 = 18/60$ of their respective axial lengths.

Using the above parameters, structure factors were calculated and Fourier projections were made upon the (001) and (100) planes (Figures 1 and 2). The centers of the peaks were located by fitting a Gaussian curve to the electron density values about the peaks (3). Observed and calculated structure factors were compared for all observed reflections. No temperature correction was applied to the calculated values because of the large carbohydrate contribution to many reflections. The discrepancy factor $R = \frac{\Sigma \| F_{obsd.}| - |F_{calcd.}\|}{\Sigma |F_{obsd.}|}$ had the values 0.46 and 0.50 for the observed (0k1) and (hk0) reflections respectively.

Discussion

Such an R factor is to be expected for appreciable carbohydrate contributions but additional evidence in favor of the parameters cited are Harker modifications of the Patterson projection prepared at intervals of 2/60 along the x axis. These sections leave no doubt concerning the iodine parameters since no major peaks occur other than those accounted for as iodine at x = 0/60 and 30/60 (Figures 3 and 4).

The structure which best accounts for the present data is a torus-like arrangement of the cyclic dextrin molecule, coaxial with and surrounding each iodine molecule. (Figure 5).

Consideration of the possible packing arrangements of the crystalline complex, as well as measurement of scale models, lead to a diameter of the torus of approximately 13.0Å and a thickness of

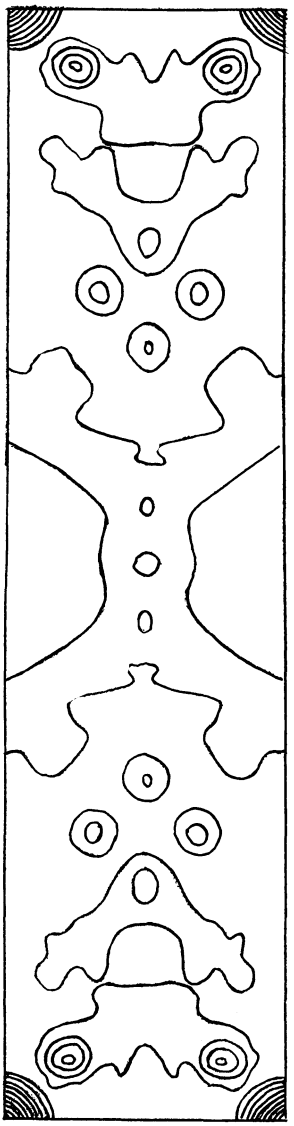

Figure 3. Patterson-Harker H(Oyz).

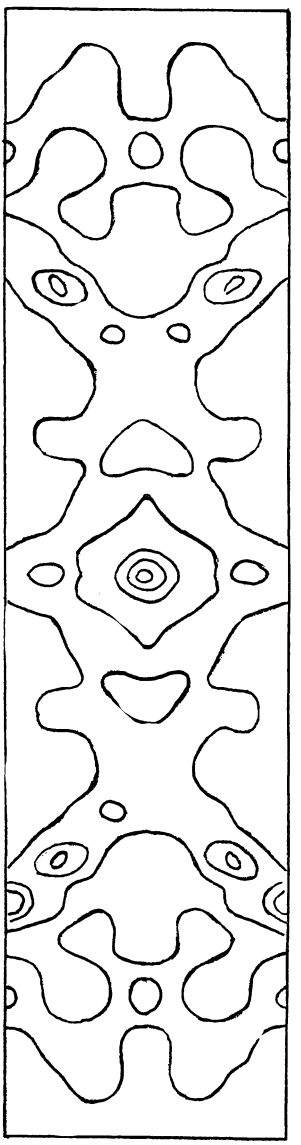

Figure 4. Patterson-Harker H(½yz).

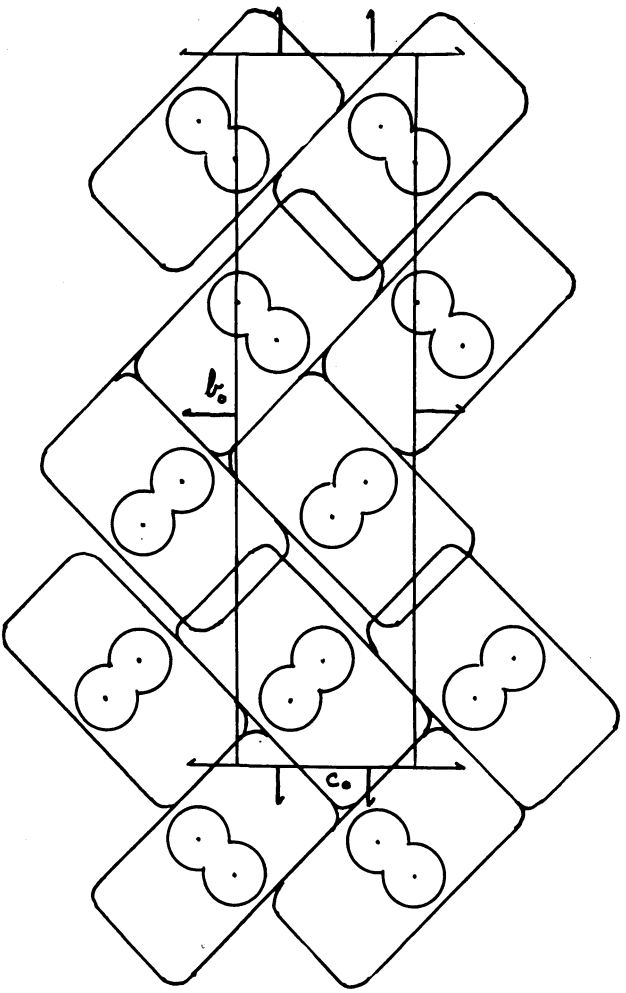

Figure 5. Packing of the Carbohydrate and Iodine Atoms on the (100) Plane.

6.8Å. Further study will be necessary to determine more exactly the arrangement of carbon and oxygen atoms in the crystal.

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References

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